

(12) **PATENT KOKAI PUBLICATION (A)** (11) Patent Kokai [laid open]

(19) Japan Patent Office (JP)

Publication Number: Kokai Hei 5-119529

(43) Publication date: Heisei 5. (1993) May 18

(51) Int.Cl. <sup>5</sup>	ID Codes	Sequence Nos. for Office Use	FI
G 03 G	9/087		
		G 03 G	9/08 381 321

Examination request: not requested yet  
Number of claims:1, (total 7 pages)

(21) Patent Application Number: Hei 3 [1991]-284281:

(22) Patent Application Date:  
Heisei 3. (1991) October 30

(71) Applicant: 000006079

Minolta Camera Co. Ltd.  
Osaka Kokusai Building, 3-13, 2-chome  
Ando-cho, Chuo-ku, Osaka-shi, Osaka-fu

(72) Inventor:

Masaaki TAKAMA  
C/o Minolta Camera Co. Ltd.  
Osaka Kokusai Building, 30-banchi,  
2-chome, Ando-cho, Higashi-ku, Osaka-fu

(72) Inventor:

Hidetoshi YOSHIDA  
Same as above

(72) Inventor

Junji MACHIDA  
Same as above

(74) Attorney:

Mikio HATTA, patent agent (includes 2 others)

(54) [Invention Title]

Toner for electrostatic charge image development  
[Seidenkazo gensoyo toner]

(57) [Abstract]

[Purpose] To improve dispersibility of colorant  
(pigment) in a toner for the development of  
electrostatic charge image given through an  
emulsifying dispersion method.

[Constitution]

It uses a grafted resin for at least part of a binder resin  
for the toner that is manufactured through an  
emulsifying dispersion method.

## [CLAIMS]

### [CLAIM ITEM 1]

According to a toner that is manufactured through by an emulsifying dispersion method, a toner for development of electrostatic charge image is characterized by the fact that uses grafted resin for at least part of a binder resin.

## [DETAILED EXPLANATION OF THE INVENTION]

### [0001]

#### [FIELD OF INDUSTRIAL APPLICATION]

This invention relates to a toner for development of electrostatic charge image. In further detail, this invention relates to the toner for development of electrostatic charge image in which dispersibility of a pigment in toner fine particles is improved.

### [0002]

#### [PRIOR ART]

An emulsifying dispersion method has been known as one method to manufacture resin fine particles. According to this method, a resin solution that is prepared by dissolving a resin in a water-insoluble organic solvent is subjected to an emulsifying dispersion in an aqueous dispersing solution to form an emulsion, and to apply heat to this emulsion while this is continued to be stirred to remove organic solvent through evaporation to give fine resin particles. According to this emulsifying dispersion method, it is possible to obtain fine polymer particles showing average particle diameter of about 1 ~ 10  $\mu\text{m}$  with a fairly simple operation of which processes are simplified; and it is not only possible to improve production efficiency compared to that of a suspension polymerization method but also, it can achieve cost reduction. In addition, types of resins that can be used are more compared to those of a pulverization method or a suspension polymerization method.

### [0003]

And therefore, when such emulsifying dispersion method is applied to compound toner components such as colorant, charge control agent, or magnetic powder and the like in a resin solution, it is anticipated possible to obtain a toner for development of electrostatic charge image that accommodates needs such as higher speed, higher image quality, and coloration that are expressed by copying machine or printer region in an electro photography method.

### [0004]

However, when an attempt is made to obtain colored fine resin particles such as a toner for development of electrostatic charge image by such emulsifying dispersion method, dispersibility of colorant (pigment) presents problems. Pigments show a strong cohesive force due to its very small particle diameter. And therefore, very large energy is required in order to disperse pigment in a resin solution; and this is generally conducted by stirring a resin solution after such pigment is added to this over long hours by using a ball mill or a sand grinder and the like. However, even when dispersion of the pigment in a resin solution is made by above-explained method, re-cohesion occurs, and it presents a concern over not uniformly dispersed pigment in thus given toner fine particles. If

colorant is not uniformly dispersed in toner fine particles, problems such as decline in charge characteristic of the toner or decline in image density and the like occur.

[0005]

Disturbance of colorant dispersion explained above is a problem that is unique to an emulsifying dispersion method. That is to say, when manufacturing toner fine particles by a kneading and pulverization method, although the colorant may show sufficiently uniform dispersed state under high pressure and the like within a kneader, a method of granulation by emulsification is known from the standpoint of manufacturing method to require a uniform dispersion of the colorant in an emulsion that is formed by emulsifying dispersion of a resin solution given by dissolving a resin in water-insoluble organic solvent in an aqueous dispersing solution. And therefore, although such problem does not occur in the case of a kneading method, above-explained uniform as uniform dispersion of colorant becomes problematic when it is in the case of emulsifying dispersion method as it requires uniform dispersion of the colorant in an emulsion.

[0006]

Furthermore, according to the publication of Japanese patent application Kokai Sho 63 [1988]-25664, at the time of manufacturing of toner fine particles by an emulsifying dispersion method, pigment is dispersed in a polymer solution by stirring for long hours using a polar solvent that is referred to as dichloromethane; and even when such polar solvent is used, it has not been possible to improve the dispersibility of pigment to the sufficient level.

[0007]

[SUBJECTS SOLVED BY THIS INVENTION]

And therefore, purpose of this invention is to offer a toner for development of electrostatic charge image. Another purpose of this invention is to offer a toner for development of electrostatic charge image when that is manufactured by an emulsifying dispersion method to allow uniform dispersion and compounding of the colorant within said fine particles. This invention also has other purpose of offering a toner for development of electrostatic charge image showing good dispersibility of the colorant that can be manufactured at low cost with good production efficiency through simple processes that utilizes said emulsifying dispersion method.

[0008]

[MEANS USED TO SOLVE THE SUBJECTS]

Above-explained purpose in the case of a toner that is manufactured through emulsifying dispersion method can be attained through a toner for development of electrostatic charge image that is characterized by using a grafted resin for at least part of a binder resin.

[0009]

[ACTIONS]

When manufacturing a toner by emulsifying dispersion method, it was found that first of all, binder resin and colorant (pigment) are dissolved or dispersed in a water-insoluble

organic solvent to adjust a colorant containing resin solution; and when a grafted resin is used for at least part of this binder resin, dispersibility of the pigment in said solution improves drastically to maintain a uniformly dispersed state of pigment in said solution with good stability over long hours in a fairly easy manner. Although detailed mechanism of that is not clear, it can be considered that most likely, cohesion of the pigment is inhibited by a steric effect of the grafted resin that is present in the solution. As explained above, according to the toner that develops electrostatic charge image that relates to this invention, and is manufactured by first forming a uniform and stable dispersed state of the pigment in colorant containing resin solution in order to form an emulsion by emulsifying and dispersing this colorant containing resin solution in an aqueous dispersing solution, and then, by removing said water-insoluble organic solvent, pigment is uniformly dispersed in toner fine particles.

[0010]

Details of this invention are explained below based on implementation examples. The toner for development of electrostatic charge image of this invention is given through an emulsifying dispersion method; and its average particle diameter is about 2 ~ 15  $\mu\text{m}$ , or more preferably, about 4 ~ 10  $\mu\text{m}$  showing uniformly dispersed pigment in the toner fine particles. And therefore, said toner shows stable resin characteristics, and in addition, of can provide a uniform image density when it is used for development by electro photography.

[0011]

Regarding binder resin that is included in this invention's toner for development of electrostatic charge image, grafted resin is used for at least part of this. Regarding grafted resins, no particular restrictions are placed as long as they can be dissolved in water-insoluble organic solvent that is used and remain insoluble or hardly soluble in water; and the ones of which grafted chain is formed through already known methods such as chain transfer method, polymer initiator method, radiation grafting method, or mechanical method and the like may be used; and it is preferable when mole ratio (branch chain/principal chain) of branch chain against principal chain is 5/95 or higher. This is because in the case of grafted resin showing under 5/95 mole ratio of branch chain against principal chain with fairly less ratio of branch chain, it presents a concern over attaining sufficient improvement effect of dispersibility of the pigment in resin solution explained above. Specific examples of grafted resin used in this invention include the followings: for instance, polymers of polyester group, polystyrene group, polyester (meth)acrylate group, styrene-ester (meth)acrylate copolymer group, styrene-(meth)acrylonitrile copolymer group, epoxy group, or polybutadiene group and the like are used as principal chains; and one or combination of more than two types of various monomers such as styrene group monomers including styrene monomer including styrene or m-methyl styrene and the like, (meth)acryl group monomer including (meth)acrylate, (meth)acryl amide, or (meth)acrylonitrile and the like, ester (meth)acrylate group monomer including methyl (meth)acrylate, ethyl (meth)acrylate, or butyl (meth)acrylate and the like, and vinyl ester group monomers including vinyl chloride or vinyl acetate and the like are graft polymerized with these to form branch chain comprising these homopolymer, random polymer, or block copolymer may be mentioned; however, it

should not at all be restricted by these. These grafted resins may be used either alone or as combination of more than two types.

[0012]

Furthermore, it is preferable when these grafted resin show 50 ~ 70 °C glass transition point (Tg), 1000 ~ 50000, or more preferably, 3000 ~ 20000 of number average molecular weight (Mn), and 2 ~60 molecular distribution (Mw/Mn) shown as the ratio of Mn and weight average molecular weight (Mw). When Tg happens to be under 50°C, heat resistance of thus given toner declines; and on the one hand, when it happens to exceed 70°C, fixing property of thus given toner declines. In addition, when Mn happens to be under 1000, high temperature offset occurs easily in the toner thus given; and on the one hand, when it happens to exceed 50000, low temperature offset occurs easily on a contrary. Furthermore, when Mw/Mn happens to be under 2, it presents a concern over a narrow non-offset region of thus given toner; and on the one hand, when it happens to exceed 60, low temperature offset occurs easily. Furthermore, in the case of toner for oil coating fixation purpose, it is more preferable when Mw/Mn is set to be 2 ~ 5; and in the case or toner for oil-free [oil less] fixation, it is preferable when Mw/Mn is set to be 20 ~ 50.

[0013]

It is all right when this invention's toner for development of electrostatic charge image, above-explained grafted resin is included in at least part of a binder resin component ; and it is possible to use one or more than two types of already known various resins that use combination of this grafted resin and styrene group resin, (meth)acryl group resin, styrene-(meth)acryl group copolymer resin, olefin group resin, polyester group resin, polyamide group resin ,carbonate resin, polyether, polyvinyl acetate group resin, polysulfone, epoxy resin, polyurethane resin or urea resin and the like that are used as binder resins for conventional toner.

[0014]

Furthermore, it is desirable when these resins besides said grafted resins also show similar glass transition point (Tg), number average molecular weight (Mn), and molecular weight distribution (Mw/Mn) as explained at the section of said grafted resins.

[0015]

Furthermore, according to this invention's toner for development of electrostatic charge image, it is all right when above-explained grafted resins are included in at least part of said binder resin component; and it is preferable when they are included at 10 weight % or more, or more preferably, 30 weight % or more based on total binder resin components. That is to say, it is because when grafted resin is included under 10 weight % based on total binder resin component, it presents a concern over uniform dispersibility of the pigment in the toner fine particles.

[0016]

Regarding colorants included in this invention's toner for development of electrostatic charge image, various types of organic or inorganic pigments with various colors shown

below may be used. That is to say, as black color pigments, carbon black, copper oxide, manganese dioxide, aniline black, active charcoal, non-magnetic ferrite, magnetic ferrite, or magnetite and the like may be mentioned. As yellow pigments, chrome yellow, zinc yellow, cadmium yellow, yellow iron oxide, mineral fast yellow, nickel titanium yellow, Naples yellow, naphthol [naphthalene] yellow S, hansa yellow G, hansa yellow 10G, benzidine yellow G, benzidine yellow GR, quinoline yellow lake, permanent yellow NCG, or tertriazine [transliteration] lake and the like may be mentioned. As orange color pigments, red chrome yellow, molybdenum orange, permanent orange GTR, pyrazolone orange, Vulcan orange, indanthrene brilliant orange RK, benzidine orange G, or indanthrene brilliant orange GK and the like may be mentioned. As red pigments, red iron oxide, cadmium red, red lead, mercury sulfide, cadmium, permanent red 4R. Lithol red, pyrazolone red, Watching red, calcium salt, lake red C, lake red D, brilliant carmine 6B, eosine lake, rhodamine lake B, alizarine lake, or brilliant carmine 3B and the like may be mentioned. As purple pigments, manganese purple, fast violet B, or methyl violet lake and the like may be mentioned. As blue pigments, iron blue, cobalt blue, alkali blue lake, Victoria blue lake, Phthalocyanine blue, non-metallic Phthalocyanine blue, partially chlorinated phthalocyanine blue, fast sky blue, or indanthrene blue BC and the like may be mentioned.

As green pigments, chromium green, chromium oxide, pigment green B, mica light-green lake, or final yellow green G and the like may be mentioned. As white pigments, zinc white, titanium oxide, antimony white, or zinc sulfide and the like may be mentioned. As extenders, baryta powder, barium carbonate, clay, silica, white carbon, talc, or alumina white and the like may be mentioned.

[0017]

Although these colorants may be used either alone or as combination of plural numbers, it is preferable when it is used generally at 1 ~ 20 parts by weight, or more preferably, at 2 ~ 15 parts by weight based on 100 parts by weight above-explained binder resin component. That is to say, when it happens to exceed 20 parts by weight, fixing property of the toner declines; and on the other hand, when it happens to be less than 1 part by weight, it presents a concern over whether or not prescribed image density can be achieved.

[0018]

It is all right to compound components, for instance, charge regulators, magnetic powder, offset inhibitor, or dye and the like as needed besides above-explained binder resin and pigment in this invention's toner for development of electrostatic charge image.

[0019]

As charge regulators, the ones that can provide either positive or negative charge by friction charging can be used without any particular restrictions; and various types of either organic or inorganic agents can be used. As positive charge regulators, for instance, Nigrosine base EX (made by Orient Kagaku Kogyo K.K.), quaternary ammonium salt P-51 (made by Orient Kagaku Kogyo K.K.), Nigrosine BONtrone N-01 [transliteration] (made by Orient Kagaku Kogyo K.K.), Sudan chief Schwarz BB

(solvent Black 3: Color Index 26150), fett Schwarz HBN (C.I. No. 26150), brilliant spirits Schwarz (made by Farben fabriken Byer Co.), zapon Schwarz X (made by Farberke Hexit Co. [transliteration]), as well as alkoxinated amine, alkyl amine, molybdenum acid chelate pigment and the like may be mentioned; and in addition, as negative charge regulators, for instance, oil black (Color Index 26150), oil black BY (made by Orient Kagaku Kogyo K.K.), BONtrone S-22 [transliteration] (made by Orient Kagaku Kogyo K.K.), salicylic acid metal complex E-81 (made by Orient Kagaku Kogyo K.K.), thio indigo group pigments, sulfonyl amine derivative of copper phthalocyanine, spirone black TRH (made by Hodogaya Kagaku Kogyo K.K.), BONtrone S-34 [transliteration] (made by Orient Kagaku Kogyo K.K.), Nigrosine SO (made by Orient Kagaku Kogyo K.K.), ceres Schwarz (R) G (made by Farben fabriken Byer Co.) , chromogen Schwarz ETOO (C.I. No. 14645), or azo oil black ® (made by National Aniline Co.) and the like may be mentioned.

[0020]

In addition, as magnetic powder, magnetite,  $\alpha$ -hematite, or various ferrite and the like may be mentioned. Furthermore, as various dyes of basic group, acid group, dispersed, or direct dye, Nigrosine, methylene blue, rose Bengal, quinoline yellow, or ultramarine blue and the like may be mentioned. In addition, as off set inhibitor used to improve fixing property of the toner, various wax, in particular, low molecular weight polypropylene, polyethylene, or polyolefin group was such as oxidation type polypropylene, or polyethylene and the like may be mentioned.

[0021]

The toner for development of electrostatic charge image of this invention is manufactured by dissolving above-explained toner components, that is to say, binder resin of which at least part is composed of grafted resin and pigment (and charge regulator, magnetic powder, dye, or offset inhibitor and the like that can be added as needed) in a water-insoluble organic solvent, and by dispersing thus given colorant containing resin solution in an aqueous dispersion solution to emulsify and disperse to form O/W type emulsion, and then, by removing said water-insoluble organic solvent from the droplets of said emulsion.

[0022]

Regarding the solvent that is used when manufacturing the toner for development of electrostatic charge image of this invention, ones that are either insoluble or difficult to dissolve in water and dissolve such binder resin that is used and explained above may be used; and for instance, benzene, toluene, xylene, methylene chloride, dichloromethane, trichloromethane, 1,2-dichloroethane, carbon tetrachloride, chloroform, diethyl ether, methyl ethyl ketone, or ethyl acetate and the like may be mentioned. These water-insoluble organic solvents may be used either alone or as combinations of more than two types.

[0023]

General device such as a ball mill, a sand grinder, or an ultrasonic wave homogenizer may be used to disperse pigment in water-insoluble organic solvent. Furthermore,

regarding the process to disperse pigment in water-insoluble organic solvent, it may be generally carried out at the same time of dissolving binder resin that at the least includes grafted resin in its one part in water-insoluble organic solvent explained earlier, or after dissolving said binder resin in water-insoluble organic solvent.

[0024]

Regarding solids concentration in this colorant containing resin solution, it must be set in such a manner so the droplets can be easily solidified as fine particles when heating O/W type emulsion that is prepared by emulsifying and dispersing this colorant containing resin solution in an aqueous dispersing solution to remove water-insoluble organic solvent from the droplets; and in particular, concentration of the polymer component in this polymer solution is set to 5 ~ 50 weight %, or more preferably, 10 ~ 40 weight %.

[0025]

Thus adjusted colorant containing resin solution is then formed as O/W type emulsion by emulsifying and dispersing in an aqueous dispersing solution. More specifically, mixed system of colorant containing resin solution and aqueous dispersing solution are sufficiently stirred by using stirring device such as a homo[geneous] mixer [blender]. Furthermore, 10 minutes or longer are considered as favorable for stirring time for this. This is because when stirring time happens to be too short, it is not possible to obtain a sharp particle diameter distribution. Regarding particle diameter of each droplet of colorant containing resin solution in the emulsion, as it directly determines size of toner fine particles, it is necessary to form droplet in accordance with the size of to-be obtained toner fine particles to provide a sufficient control over its particle diameter distribution.

[0026]

In addition, ratio of volume ( $V_p$ ) of colorant containing resin solution and volume of aqueous dispersing solution ( $V_v$ ) when adjusting O/W type emulsion is  $V_p/V_v \leq 1$ , or more preferably, within a range of  $0.3 \leq V_p/V_v \leq 0.7$ . That is to say, when it happens to be  $V_p/V_v > 1$ , stable O/W type emulsion cannot be formed to present a large concern over either causing phase transition in the middle of process or forming of W/O type emulsion.

[Note: Subscript of  $V_p$  and  $V_v$  need to be verified [poor print copy]. Translator's note]

[0027]

Regarding aqueous dispersing solution that is used to form O/W type emulsion, water can be used basically; and it is all right to include water-soluble organic solvent at the rate that does not breakdown emulsion. For instance, water, water/methanol mixture solution (weight ratio 50/50 ~ 100/0), water/ethanol mixture solution (weight ratio 50/50 ~ 100/0), water/acetone mixture solution (50/50 ~ 100/0), or water/methyl ethyl ketone mixture solution (weight ratio 70/30 ~ 100/0) and the like may be used.

[0028]

In addition, when forming such O/W type emulsion, it is all right to add dispersion stabilizer or auxiliary dispersion stabilizer as needed. Dispersion stabilizer has



hydrophilic colloid property in an aqueous dispersing solution; and in particular, gelatin, gum Arabic, agar-agar, cellulose derivative (for instance, hydroxy methyl cellulose, hydroxy ethyl cellulose, or hydroxy propyl cellulose and the like), synthetic polymers (polyvinyl alcohol, polyvinyl pyrrolidone, polyacryl amide, polyacryl acid salt, or polymethacrylic salt and the like) may be mentioned. In addition, auxiliary dispersion stabilizer, surfactants are generally used; and natural surfactant such as saponin; nonion group surfactants such as alkylene oxide group, glycerol group, or glycydol group and the like may be mentioned; and anion group surfactants such as carboxylic acid, sulfonic acid, phosphoric acid, ester sulfate group, or ester phosphate group and the like may be mentioned. Particularly favorable combination of dispersion stabilizer and auxiliary dispersion stabilizer include cellulose derivative (methyl cellulose group derivative) and anion group surfactant (dodecyl benzene sodium sulfonate), or polyvinyl alcohol and anion group surfactant.

[0029]

After forming O/W type emulsion in the manner explained above, temperature is gradually raised over the entire system to totally remove water-insoluble organic solvent in the droplets to form toner fine particles. Or else, it is all right to spray O/W type emulsion into dry atmosphere to totally remove water-insoluble organic solvent in the droplets to form toner fine particles while evaporating and removing aqueous group dispersant as well. Regarding dry atmosphere to which O/W type emulsion is sprayed, various gasses heated to 20°C to 250°C such as air, nitrogen, carbon acid gas, or combustion gas and the like may be generally used. After forming toner fine particles in above-explained manner, they may be put through processes such as rinsing, drying or classification and the like as needed to give toner for development of electrostatic charge image showing a sharp particle diameter distribution relating to this invention.

[0030]

[EXAMPLES]

This invention is more specifically explained below in reference with examples.

[0031]

EXAMPLE 1

[Table 1]

COMPONENTS	PARS BY WEIGHT
Polyester resin (no grafting, 123°C softening point, 65°C Tg, AV 23, OHV 40)	80
Polyester-styrene-acryl resin (grafted resin) (poly(styrene/acryl) chain is grafted to polyester principal chain, polyester/poly(styrene/acryl) = 95/5 (mole ratio), 90°C softening point, 61°C Tg, Mn=5400, Mw/Mn = 5.8)	20
Phthalocyanine pigment (average particle diameter 0.1 μm)	5

Above-explained materials were added to 500 parts by weight methylene chloride; and it was treated for 10 minutes by using an ultrasonic wave homogenizer (output 400  $\mu$ A) to dissolve and disperse above-explained materials in a solvent. Liquid-form mixture system of post-ultrasonic wave treatment was visually observed to evaluate dispersion state of the pigment based on the reference of 4 steps shown below. Results are shown in the Table 2. Furthermore, thus given liquid-form mixture is identified as colorant containing resin solution 1. On the one hand, 1 part by weight of hydroxy propyl methyl cellulose (Metorose 65SH-50 [transliteration] made by Shinetsu Kagaku K.K.) and 1 part by weight sodium dodecyl sulfate were dissolved in 100 parts by weight water; and this is identified as dispersing solution 1. While 100 parts by weight of dispersing solution 1 was stirred in a homo-mixer (made by Tokushukika Kogyo K.K.) at 3000 rpm, 50 parts by weight of above-explained colorant containing resin solution was dropped. After completion of said dropping, it was further stirred for 10 minutes at the same rpm, and then, while holding liquid temperature at 40°C, it was gently stirred at 500 rpm with a three one motor to evaporate and remove methylene chloride from the droplets by in-liquid drying method. After methylene chloride was totally removed, thus given colored fine particles were rinsed, dried, and classified to give colored fine particles 1 showing 11  $\mu$ m volume average particle diameter. Thus given colored fine particles 1 were used as a toner, and image density evaluation was conducted by the method explained later. Results are shown in the Table 2.

[0032]

#### EXAMPLE 2

Liquid-form mixture was adjusted in the same manner as explained in the example 1 by not using polyester resin and setting the application rate of grafted resin to 100 parts by weight; and this is identified as colorant containing resin solution II. Dispersion state of the pigment in this colorant containing resin solution II was evaluated in the same manner as explained in the example 1. Results are shown in the Table 2. Furthermore, colored fine particles showing 11  $\mu$ m volume average particle diameter were prepared in the same manner as explained in the example 1 by using above-explained colorant containing resin solution II in the place of colorant containing resin solution I; and this is identified as colored fine particles II. Thus given colored fine particles II were used as atoner, and image density evaluation was conducted in the same manner as explained in the example 1. Results are shown in the Table 2.

[0033]

#### EXAMPLE 3

Liquid-form mixture was adjusted in the same manner as explained in the example 1 by using methylene chloride/toluene mixture solution (weight ratio 2/8) in the place of methylene chloride as a solvent; and this is identified as colorant containing resin solution III. Dispersion state of the pigment in this colorant containing resin solution III was evaluated in the same manner as explained in the example 1. Results are shown in the Table 2. Furthermore, colored fine particles showing 11  $\mu$ m volume average particle diameter was prepared in the same manner as explained in the example 1 by using above-explained colorant containing resin solution III in the place of colorant containing resin

solution I, and changing heat retention temperature during solvent removal treatment to 60°C from 40°C. This is identified as colored fine particles III. Thus given colored fine particles III were used as a toner, and image density evaluation was conducted in the same manner as explained in the example 1. Results are shown in the Table 2.

[0034]

#### EXAMPLE 4

Liquid-form mixture was adjusted in the same manner as explained in the example 1 by changing mole ratio of principal chain and bran chain of grafted resin to (polyester/poly(styrene-acryl))=80/20 (88°C softening point, 60°C Tg, Mn=5100, Mw/Mn=5.2). This is identified as colorant containing resin solution IV. Dispersion state of the pigment in this colorant containing resin solution IV was evaluated in the same manner as explained in the example 1. Results are shown in the Table 2. Furthermore, colored fine particles showing 11 µm volume average particle diameter were prepared in the same manner as explained in the example 1 by using above-explained colorant containing resin solution IV in the place of colorant containing resin solution I; and this is identified as colored fine particles IV. Thus given colored fine particles IV were used as a toner, and image density evaluation was conducted in the same manner as explained in the example 1. Results are shown in the Table 2.

[0035]

#### EXAMPLE 5

Liquid-form mixture was adjusted in the same manner as explained in the example 2 by changing Phthalocyanine pigment to 8 parts by weight carbon black (MA#8 made by Mitsubishi Kasei K.K.); and this is identified as colorant containing resin solution V. Dispersion state of the pigment in this colorant containing resin solution V was evaluated in the same manner as explained in the example 1. Results are shown in the Table 2. Furthermore, colored fine particles showing 11 µm volume average particle diameter were prepared in the same manner as explained in the example 1 by using above-explained colorant containing resin solution V in the place of colorant containing resin solution II, and this is identified as colored fine particles V. Thus given colored fine particles V were used as a toner, and image density evaluation was conducted in the same manner as explained in the example 1. Results are shown in the Table 2.

[0036]

#### EXAMPLE 6

Liquid-form mixture was adjusted in the same manner as explained in the example 2 by changing type of grafted resin used to polybutadiene-styrene-acrylonitrile resin (grafted resin) (poly(styrene-acrylonitrile) chain is grafted to polybutadiene principal chain, polybutadiene/poly(styrene-acrylonitrile)= 90/10 (mole ratio), 124°C softening point, 70°C Tg, Mn=11000, Mw/Mn=15.4); and this is identified as colorant containing resin solution VI. Dispersion state of the pigment in this colorant containing resin solution VI was evaluated in the same manner as explained in the example 1. Results are shown in the Table 2. Furthermore, colored fine particles showing 11 µm volume average particle diameter were prepared in the same manner as explained in the example 1 by using above-explained colorant containing resin solution VI in the place of colorant containing

resin solution I; and this is identified as colored fine particles VI. Thus given colored fine particles VI were used as a toner, and image density evaluation was conducted in the same manner as explained in the example 1. Results are shown in the Table 2.

[0037]

#### COMPRATIVE EXAMPEL 1

Liquid-form mixture was adjusted in the same manner as explained in the example 1 by not using grafted resin and setting application rate of polyester resin to 100 parts by weight, and this is identified as colorant containing resin solution VII. Dispersion state of the pigment in this colorant containing resin solution VII was evaluated in the same manner as explained in the example 1. Results are shown in the Table 2. Furthermore, colored fine particles showing 11  $\mu\text{m}$  volume average particle diameter were prepared in the same manner as explained in the example 1 by using above-explained colorant containing resin solution VII in the place of colorant containing resin solution I, and this is identified as colored fine particles VII. Thus given colored fine particles VII were used as a toner, and image density evaluation was conducted in the same manner as explained in the example 1. Results are shown in the Table 2.

[0038]

#### COMPARATIVE EXAMPLE 2

Liquid-form mixture was adjusted in the same manner as explained in the comparative example 1 by using toluene in the place of methylene chloride as a solvent, and this is identified as colorant containing resin solution VIII. Dispersion state of the pigment in this colorant containing resin solution VIII was evaluated in the same manner as explained in the example 1. Furthermore, colored fine particles showing 11  $\mu\text{m}$  volume average particle diameter were prepared in the same manner as explained in the example 1 by using above-explained colorant containing resin solution III [note: although original document states solution III, it may be a misprint of VIII. Translator's note] in the place of colorant containing resin solution I, and changing heating retention temperature during solvent removal treatment to 60°C from 40°C, and this is identified as colored fine particles VIII. Thus given colored fine particles VIII were used as a toner, and image density was evaluated in the same manner as explained in the example 1. Results are shown in the Table 2.

[0039]

#### EVALUATION METHOD

##### 1) EVALUATION ON DISPERSION STATE OF PIGMENT

Dispersion state of pigment in colorant containing resin solution after dispersion by ultrasonic wave was evaluated based on the following 4 steps:

- OO : no cohesion of pigment is noted
- O : some cohesion of pigment is noted
- $\Delta$  : fair amount of cohesion of pigment is noted
- X : hardly any dispersion is noted

##### 2) EVALUATION ON IMAGE DENSITY

First of all, colored resin fine particles given through examples 1 ~ 6 and comparative examples 1 ~ 2 were mixed with carrier that provides appropriate charge rate to said colored resin fine particles; and commercially available copying machine (EP410Z made by Minolta Camera K.K.) was used to develop electrostatic image, and that was transferred and fixed on an ordinary paper. During imaging and fixing, image showing 0.6  $\mu\text{m}/\text{cm}^2$  adhesion rate was selected to measure image density by using Sakura Densitometer. Furthermore, amber filter was used for the one by example 5, and red filter was used for the remaining examples.

[0040]

[Table 2]

	DISPERSIBILITY OF PIGMENT	IMAGE DENSITY
Example 1	OO	1.4
Example 2	OO	1.6
Example 3	OO	1.4
Example 4	OO	1.6
Example 5	OO	1.4
Example 6	OO	1.4
Comparative example 1	$\Delta$	1.1
Comparative example 2	X	0.9

[0041]

As it is clear from the results shown in Table 2, the ones relating examples 1 ~ 6 of this invention show good pigment dispersibility in colorant containing resin solution, and it can be considered that the pigment dispersion on thus given colored resin fine particles is also good, and image density on fixed image is high. To this, the ones of comparative examples 1 ~ 2 show low image density on fixed image due to poor dispersibility of pigment.

[0042]

[EFFECTS OF THIS INVENTION]

As explained above, according to the toner that is manufactured through emulsifying and dispersion method, this invention provides a toner for development of electrostatic charge image that is characterized by the fact that uses grafted resin in at the least part of binder resin to show good dispersibility of colorant (pigment) in toner fine particles; and image density of fixed image when electrostatic charge image is developed remains high and sufficient; and furthermore, charge characteristics of the toner also become excellent.